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Influence of annealing on the structure and optical properties of $Zn_{40}Se_{60}$ thin films

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ABSTRACT

Thin films of $Zn_{40}Se_{60}$ were prepared by the vacuum thermal evaporation technique. The influence of annealed temperature on the structural and optical properties was investigated using the X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical transmission. The XRD studies show that the as-deposited film is amorphous in nature, but the crystallinity improved with increasing the annealing temperature. Furthermore the particle size and crystallinity increased whereas the dislocation and strains decreased with increasing the annealing temperature. SEM studies showed that the annealing temperature induced changes in the morphology of the as-deposited sample. Various optical constant have been calculated for as-deposited and annealed films. The mechanism of the optical absorption follows the rule of direct transition. It was found that, the optical energy gap (E_g) decreased with increasing the annealing temperature. These results can be interpreted by the Davis and Motte model. On the other hand the maximum value of the refractive index (n) is shifted toward the long wavelength by increasing the annealing temperature.

1. Introduction

The growth of the groups II–VI semiconductors has attracted considerable attention because of their novel physical properties and many applications in optoelectronic devices. One of these compounds is Zinc Selenide (ZnSe) with cubic Zinc-blend structure and with a direct band gap of about 2.7 eV at room temperature. Zinc selenide (ZnSe) has unique physical properties such as wide optical energy band gap, high refractive index and low optical absorption in the visible and infrared spectral region [1]. On the other hand, the zinc selenide has several potential applications in devices such as blue light emitting diodes [2,3] photodiodes [4], thin film transistors [5] and Cr doped ZnSe laser [6]. The zinc selenide is also used as buffer layer materials instead of CdS in Cu based solar cells [7,8]. The advantages of using ZnSe over CdS include its non-toxicity, its wider energy band gap than CdS.

Zinc selenide thin films have been prepared by various techniques such as thermal evaporation under vacuum, molecular beam epitaxy, organo-metallic chemical vapor deposition, solution growth spray pyrolysis etc. [9–12]. Among the various techniques, the vacuum thermal evaporation is very common due to its simplicity, low cost reproducibility and scalability deposit onto large area substrates. Moreover, the films produced with this method are highly adherent and uniform. On the other hand, the structural, electrical and optical properties of thin films are very sensitive to deposition conditions and post-deposition heat treatments [13–16].

The present work deals with some experimental observation on the effect of heat treatment on structure and optical properties of $Zn_{40}Se_{60}$ films. Scanning electron microscopy (SEM) and X-ray diffraction were used to determine the structural changes for $Zn_{40}Se_{60}$ films under different conditions. The effect of thermal annealing on optical properties is interpreted according to the density of states model in amorphous materials proposed by Mott and Davis [17]. In this paper, we report the study of the dependence of the optical properties of the $Zn_{40}Se_{60}$ thin films on annealing temperature.

2. Experimental details.

Bulk $Zn_{40}Se_{60}$ was prepared by the melt-quench technique. Appropriate amounts of high purity (99.999%) Zn and Se (from Aldrich, UK) were weighted (5 g total weight) according to their atomic percentage. The weighted elements were placed into a quartz glass ampoule and sealed under vacuum of 10^{-4} Torr. The sealed ampoule was heated in Heraus programmable tube furnace (type R 07115), the heating rate was approximately 3.5 K/min. The temperature was kept at 1073 K for 24 h. The

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ampoule was manually stirred for realizing the homogeneity of the composition. After that, the ampoule was quenched into ice-cooled water.

Thin films were prepared by thermal evaporation under vacuum of 10^{-5} Torr using the Edwards E-306 coating system. A constant evaporation rate (3 nm/sec) was used to deposit the films. The evaporation rates as well as the films thickness were controlled using a quartz crystal monitor (FTM5). The film composition was checked using the energy-dispersive spectroscopy (EDAX) technique.

$Zn_{40}Se_{60}$ films were annealed at different temperature ($373 \leq T_{ann} \leq 423$ K) for half hour under gas Nitrogen. The morphology for as-deposited and annealed films were investigated using (SEM) type JEOL JSM-T200. The crystalline phases for as-prepared and annealed films were identified using a Philips diffractometer type 1710.

The optical transmittance (T) and reflectance (R) of the as-deposited and annealed $Zn_{40}Se_{60}$ films were measured at room temperature using a double-beam spectrophotometer (SHIMADZU UV-2101 combined with a PC) in the wavelength 300–900 nm.

3. Results and discussion

3.1. Structure studies

The composition of $Zn_{40}Se_{60}$ thin films was investigated using energy dispersive X-ray analysis (EDAX). The atomic percentage ratio of Zn and Se were found to be 38.25 and 61.75, respectively, as shown in Fig. 1.

The morphology of the annealed $Zn_{40}Se_{60}$ thin films was examined using SEM. The scanning micrograph of the annealed $Zn_{40}Se_{60}$ films are shown in Fig. 2(a, b). The microstructure for the annealed sample at 373 K for 0.5 h are shown in Fig. 2(a), the photomicrograph shows the existence of polycrystalline structures consisting of crystallites embedded in amorphous phases. The crystalline morphology is not distinct due to the fact that the crystallization is only in its initial stages. On the other hand, the scanning electron micrograph for the annealed $Zn_{40}Se_{60}$ thin films at 423 K for 0.5 h is shown in Fig. 2(b). A polycrystalline structure consists of different phases with different sizes appears. In general the crystallites are dispersed homogenously and occupy most of the film structure.

In order to determine the crystalline phases that appeared in SEM for the annealed $Zn_{40}Se_{60}$ thin films, the X-ray diffraction pattern of films were analyzed. Fig. 3(a–c) shows XRD pattern of the as-deposited and annealed $Zn_{40}Se_{60}$ films. The XRD studies show that the as-deposited film is amorphous in nature as shown in Fig. 3(a) but the film annealed at 373 K shown in Fig. 3(b) did not show significant improvement in crystallinity. On the other hand the XRD peaks of the film annealed at 423 K, shows increase in intensity of the diffraction peaks that corresponds to the cubic phase along with appearance of new peaks that corresponds to Se phase formed as shown in Fig. 3(c).

The average of crystalline size D were calculated using Scherer's formula [18].

$$D = 0.94\lambda/\beta\cos\theta, \quad (1)$$

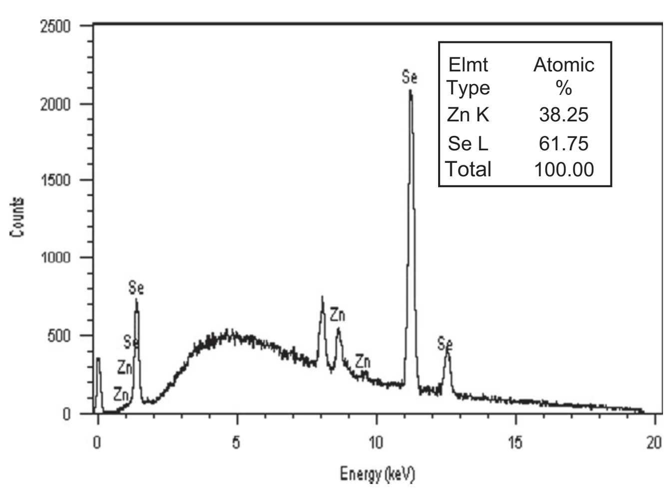

Fig. 1. Typical EDAX of as-deposited $Zn_{40}Se_{60}$ thin films.

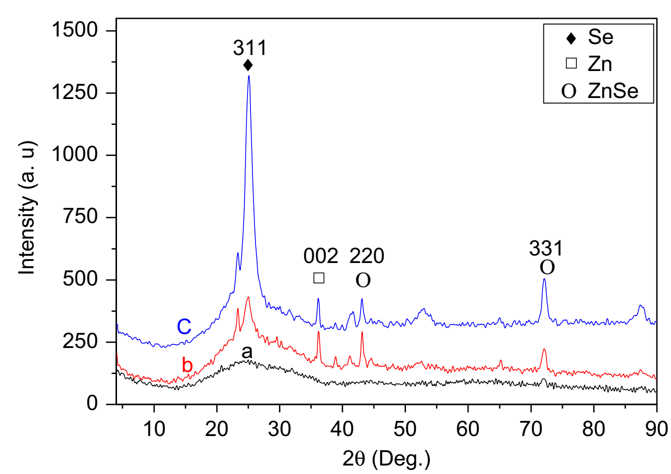

Fig. 3. The X-ray patterns of $Zn_{40}Se_{60}$ thin films, (a) as-deposited (b) annealed at 373 K and (c) annealed at 423 K.

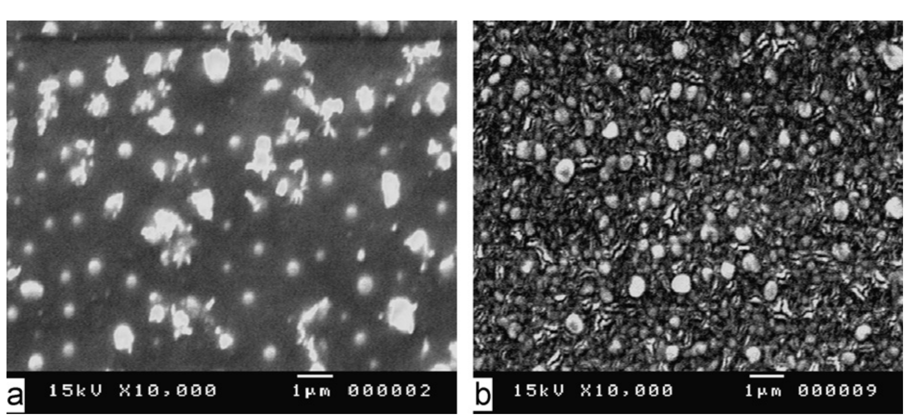

Fig. 2. The SEM photograph for $Zn_{40}Se_{60}$ thin films (a) annealed at 373 K and b annealed at 423 K.